Chapter 1
Introduction

Abstract The properties of a material are a direct result of its internal structure. The ability to control structures through processing, and to develop new structures through various techniques, requires qualitative and quantitative analysis of the atomic and electronic structure. The average and local structure of some significant metals and important alloys have been analyzed and reported in this book. This introduction chapter deals with the significance and applications of metals, alloys and semiconductors. The essential mechanism of ball milling which has evolved to be a simple and useful method for the formation of nano crystalline materials is discussed. The current state-of-the-art of non-destructive characterisation techniques such as X-ray diffraction and scanning electron microscope are discussed.

1.1 Introduction

The development of improved metallic materials is a vital activity at the leading edge of science and technology. Metals offer various combinations of properties and reliability at a cost which is affordable. They are versatile because subtle changes in their microstructure can cause dramatic variations in their properties. An understanding of the development of microstructure in metals, rooted in thermodynamics, crystallography and kinetic phenomena is essential for the materials scientist.

Alloys can blend the properties of two or more metals to create a hybrid metal that is more cost-effective, stronger, more durable and overall better suited to its intended purpose than the pure metals used to create the compound. With emerging requirement of designing new materials capable of sustaining high-strain rate and severe operating conditions with reduced wastage of cost, energy and material, it has become an important issue to develop full understanding of

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the nature of enhanced mechanical properties of the materials. New materials that can be tailored for individual applications are always in a constant demand. As the range of uses for powder metallurgy, hard metals and electronic materials expands, customer requirements are causing materials companies to come up with new products that have the required properties.

1.2 Significance of the Present Work

Metals and semiconductors play an important role in the present world as evidenced by their variety of applications. Hence, a study on some important metals, alloys and semiconducting systems is essential in terms of the local structure and the average structure which are completely different. The usual methods of analysis using structural refinement of X-ray or neutron data will give only the average structure of the materials under investigation. The studies on the local structure of materials seem to be rare because of the complexity of the problem. There is only limited information available about the investigations of materials in terms of the local structure. Numerous research papers are being published every year based on powder as well as single-crystal X-ray diffraction (XRD) data. The structures reported using those data are only average structures. Since, the analysis of local structure requires highly precise data up to maximum possible Bragg angle, accurate refinement of the data is limited. Due to the complexity of the problem, tasks of acquirement of precise X-ray data from the samples, and the computational incapabilities, local and average structural analysis has not been much explored. Atomic ordering is closely related to the materials' electronic and magnetic properties. Although the physical properties of alloys are closely related to their electronic structures, studies on the charge transfer and hybridisation of the electronic states are still insufficient (Lee et al. 2004).

In the present monograph, apart from pure metals, investigations on the local and average structures of doped metals and alloys are carried out with various doping concentrations. The average structure has been studied using both single-crystal and powder XRD data in some cases. The bonding and electron density distribution of the host as well as dopant atoms have been studied using tools like maximum entropy method (MEM) (Collins 1982) and multipole analysis (Hansen and Coppens 1978). For powder analysis, Rietveld refinement technique (Rietveld 1969) (for average structure) and Pair Distribution Function (Proffen and Billinge 1999) (for local structure) have been used. Effects on the electron density distribution by ball milling (El-Eskandarany 2001; Suryanarayana 2004; Ares et al. 2005) of alloy has been analyzed in this work.

The present research work reveals the local and average structural properties of some technologically important materials, which are not studied in these lines. New understandings of the existing materials have been gained in terms of the local structure and average structure of the materials. The electron density, bonding and charge transfer studies analyzed in this work would give fruitful

information to researchers in the fields of physics, chemistry, materials science, metallurgy, etc. These properties can be properly utilised for the proper engineering of these technologically important materials.

1.3 Objectives

Though the materials studied and reported in this research book are all metals and alloys, the work has been divided into several parts for the sake of convenience. They have been given as below.

1. The average and electronic structure of the following elemental metals using Rietveld (Rietveld 1969), multipole (Hansen and Coppens 1978) and MEM (Collins 1982) by single-crystal XRD data.
   - Sodium (Na)
   - Vanadium (V)
2. a. The local, average and electronic structure of the following elemental metals using Rietveld (1969), and MEM (Collins 1982) by powder XRD data.
   - Magnesium (Mg)
   - Aluminium (Al)
   - Titanium (Ti)
   - Iron (Fe)
   - Nickel (Ni)
   - Copper (Cu)
   - Zinc (Zn)
   - Tin (Sn)
   - Tellurium (Te)

   b. The local structural information by analyzing the atomic pair distribution function (PDF) (Proffen and Billinge 1999).
3. The average and electronic structure of the following metal alloys using multipole (Hansen and Coppens 1978) and MEM (Collins 1982) by single-crystal XRD data.
   - cobalt aluminium (CoAl)
   - nickel aluminium (NiAl)
   - Iron nickel (FeNi)
4. a. The annealing and ball milling of the alloy nickel chromium ($Ni_{80}Cr_{20}$)
   b. The study of the local, average and electronic structure of the annealed and ball milled alloy $Ni_{80}Cr_{20}$ using Rietveld (Rietveld 1969) and MEM (Collins 1982) by powder XRD data.
   c. To study the local structure using PDF (Proffen and Billinge 1999).

d. Analysis of the particle sizes of the differently treated samples by scanning electron microscopy (SEM) and (XRD).

5. The study of the average and electronic structure of the following doped alloys using Rietveld (1969), multipole (Hansen and Coppens 1978) and MEM (Collins 1982) by single-crystal XRD data.

- Sodium chloride with iron impurities ($Na_{1-x}Ag_xCl$)
- Aluminium, with iron impurities (0.215 wt% Fe and 0.304 wt% Fe)

1.4 Metals

Metals account for about two-thirds of all the elements and about 24% of the mass of the planet. Metals have useful properties including strength, ductility, high-melting points, thermal and electrical conductivity and toughness. The key feature that distinguishes metals from nonmetals is their bonding. (Gallagher and Ingram 2001) Metallic materials have free electrons that are free to move easily from one atom to the next. The existence of these free electrons has a number of profound consequences in the properties of metallic materials (Kittel 2007).

The local and average structures of some technologically important metals such as sodium, magnesium, aluminium, titanium, vanadium, iron, nickel, copper, zinc, tin and tellurium are analyzed in this work and their typical properties and uses are presented below.

1.4.1 Sodium

Sodium is a soft, silvery-white, highly reactive metal having only one stable isotope; ^{23}Na. Sodium ion is soluble in water in nearly all of its compounds. Sodium metal is so soft that it can be cut with a knife at room temperature (Zumdahl 2007)

Sodium compounds are important for the chemical, glass, metal, paper, petroleum, soap, and textile industries. A sodium–sulphur battery is a type of molten metal battery constructed from sodium and sulphur. This type of battery has a high-energy density, high efficiency of charge/discharge (89–92%) and long cycle life, and is fabricated from inexpensive materials (Oshima et al. 2004). NaS batteries are a possible energy storage technology to support renewable energy generation, specifically in wind farms and solar generation plants. In the case of a wind farm, the battery would store energy during times of high wind but low-power demand. This stored energy could then be discharged from the batteries during peak load periods. In addition to this power shifting, it is likely that sodium sulfur batteries could be used throughout the day to assist in stabilising the power output of the wind farm during wind fluctuations (Walawalkar et al. 2007). Due to its high-energy density, the NaS battery has been proposed for space applications (Auxer 1986).

1.4.2 Vanadium

Pure vanadium is a bright white metal, and is soft and ductile. It has good corrosion resistance to alkalis, sulphuric and hydrochloric acid and salt water. The metal has good structural strength and a low fission neutron cross section, making it useful in nuclear applications. (Lynch 1974).

Vanadium is used in producing rust resistant, spring and high-speed tool steels. It is an important carbide stabiliser in making steels. Vanadium is also used in producing superconductive magnets with a field of 175,000 gauss (Lide 1999).

The role of vanadium complexes in catalytically conducted redox reactions (Crans et al. 2004) and potential medicinal applications, such as in the treatment of diabetes type I and type II (Crans 2000), has stimulated interest in the stereochemistry and reactivity of its coordination compounds (Monfared et al. 2010).

Vanadium oxides and vanadium oxide-related compounds have a wide range of practical applications such as catalysts, gas sensors and cathode materials for reversible lithium batteries, electrochemical and optical devices, due to their structural, novel electronic and optical properties (Zhang et al. 2010). Mixed metal oxides find applications in a variety of fields due to the wide variation in their dielectric and electrical properties. The vanadium-based oxide ceramics have high-dielectric constant, low-dissipation factor and high-quality factor, which favour the use of these ceramics in many fields (Nithya and Kalaiselvan 2011).

Secure and reliable power is essential in areas such as telecommunications and information technology to safeguard the vast computer networks that have been established. Uninterruptible power systems have incorporated battery technology to allow smooth power feeding switch-over in the case of a power failure. In such systems lead-acid batteries are commonly being used until generators come online or for safe computer shutdown. The vanadium redox battery provides many advantages over conventional batteries for emergency back-up applications. This system stores all energy in the form of liquid electrolytes which are re-circulated around the battery system. The electrolytes can be recharged for indefinite number of times, or the system can be instantly recharged by mechanically exchanging the discharged solution with recharged solution (Kazacos and Menictas 1997).

Figure 1.1 shows a vanadium redox battery. A vanadium redox battery consists of a power cell in which two electrolytes are kept separated by an ion exchange membrane. Both the electrolytes are vanadium based. Vanadium redox batteries are based on the ability of vanadium to exist in four different oxidation states (V_2, V_3, V_4 and V_5), each of which holds a different electrical charge. The electrolyte in the negative half-cell has V_3^+ and V_2^+ ions, while the electrolyte in the positive half-cell contains V_3^+ and V_2^+ ions. During charging, reduction in the negative half-cell converts the V_3^+ ions into V_2^+ ions. During discharge, the process is reversed, oxidation in the negative half-cell converts V_2^+ ions back to V_3^+ ions. The typical open-circuit voltage created during discharge is 1.30 V at 25°C (Skyllas-Kazacos 2003).

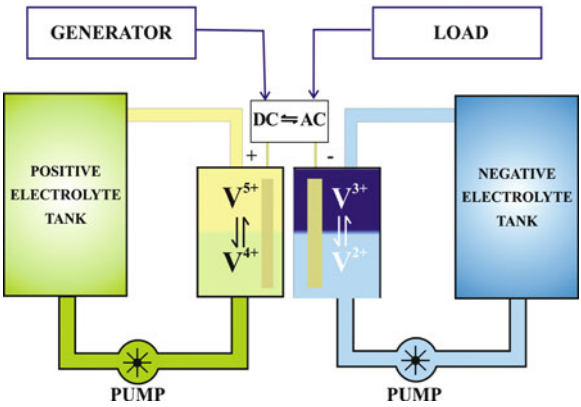

Fig. 1.1 Vanadium redox battery

Other useful properties of Vanadium flow batteries are their quick response to changing loads and their extremely large overload capacities. Their extremely rapid response times also make them perfectly well suited for UPS-type applications, where they can be used to replace lead-acid batteries and even diesel generators.

1.4.3 Magnesium

Elemental magnesium is a fairly strong, silvery-white, light-weight metal. The lightness combined with good strength-to-weight ratio has made magnesium and its alloys suitable for use in missiles and automotive industry.

Magnesium alloys have low density (1.5–1.8 g/cm^3) and high strength in relation to their weight (Kainer 2000). Magnesium alloys are used for die-casting due to their good corrosion resistance and low heat of fusion with the mould material. Most of the magnesium alloy castings are made for the automotive industry. Lowering car weight by 100 kg makes it possible to save 0.5 l petrol/100 km. It is anticipated that in the following years the mass of castings from magnesium alloys in an average car will rise to 40 kg, internal combustion engines will be made mostly from the magnesium alloys and car weight will decrease from 1,200 to 900 kg (Mordike and Ebert 2001a, b).

A good capability of damping vibrations and low inertia connected with a relatively low weight of elements have predominantly contributed to the employment of magnesium alloys for the fast moving elements and in locations where rapid velocity changes occur; some good examples may be car wheels, combustion engine pistons, high-speed machine tools and aircraft equipment elements (Wang et al. 2002).

The concrete examples for the use of castings of magnesium alloys in batch production in the automotive industry are elements of the suspension of the front

and rear axes of cars, propeller shaft tunnel, pedals, dashboards, elements of seats, steering wheels, elements of timer-distributors, air filters, wheel bands, oil sumps, elements and housings of the gearbox, framing of doors and sunroofs and others (Dobrzánski et al. 2007).

In recent times, the increased environmental concerns and the rising costs of oil have again made magnesium and its alloys a material of interest for the automotive industry. Considering the characteristics of low density of magnesium, its extensive use in structural body parts of vehicles will offer major reductions of weight and hence reduction in fuel consumption. Such weight reduction provides a significant contribution to reducing the carbondioxide emission. It is estimated that an average new car produces 156 g CO_2/km travelled. This could be reduced to around 70 g CO_2/km through the application of magnesium technology (Mehta et al. 2004).

The advantages of magnesium and magnesium alloys are, lowest density of all metallic constructional materials, high-specific strength, good castability, suitable for high-pressure die-casting, can be turned or milled at high speed, good weldability under controlled atmosphere, much improved corrosion resistance, readily available, better mechanical properties, resistant to ageing, better electrical and thermal conductivity and recyclability (Mordike and Ebert 2001a, b).

Magnesium alloys have attracted increasing interest in the past few years due to their potential as implant materials. Magnesium and its alloys are degradable during their time of service in the human body. Magnesium alloys offer a property profile that is very close or even similar to that of human bone (Hort et al. 2010).

1.4.4 Aluminium

Aluminium has been the dominant material in the aircraft industry for more than a half century due to its attractive combination of light weight, strength, ductility, corrosion resistance, ease of assembly and low cost (Dorward and Pritchett 1988). Aluminium foam sandwiches (AFS) due to their flexible process ability and potential of cost reduction find application in space components. Currently, these light-weight materials find some first applications in particular fields of mechanical engineering such as race cars, and small series of other land-based vehicles (Schwingel et al. 2007). The use of high-strength aluminium alloys in automotive and aircraft industries allows reducing significantly the weight of the engineering constructions. In these fields, very often the main requirements for the components include high fatigue and wear-resistance (Lonyuk et al. 2007). Aluminium solar mirrors are an alternative for solar concentrators. The aluminium reflectors often offer an initial reflectance of 85–91% for solar irradiance. They have good mechanical properties and are easy to recycle (Almanza et al. 2009). The high strength-to-weight advantage of aluminium alloys has made it the material of choice for building airplanes and sometimes for the construction of land-based structures. For marine applications, the use of high-strength, weldable and

corrosion-resistant aluminium alloys have made it the material of choice for weight sensitive applications such as fast ferries, military patrol craft and luxury yachts and to lighten the top-sides of offshore structures and cruise ships (Paik et al. 2005).

1.4.5 Titanium

Titanium has many desirable physical properties. The pure metal is relatively soft and weak, but it becomes much stronger when mixed with other metals to form alloys. The high-melting point of titanium (1,668°C) shows that it is an ideal material for the construction of high-speed aircraft and space vehicles.

Due to the exceptional strength-to-weight ratios, toughness, high stiffness and excellent biocompatibility, titanium and its alloys are used extensively in aerospace, chemical and biomedical applications (Kartal et al. 2010). Titanium alloys are widely used in the aerospace industry due to their excellent fatigue/crack propagation behaviour, and corrosion resistance (Markovsky and Semiatin 2010). The alloys of titanium represent significant advantages over most other engineering materials used for a variety of industrial applications due to their resistance to corrosion, oxidation and erosion. Titanium and its alloys have high-chemical durability as well as high strength. Their use is significant in nuclear industry, since the mechanical strength, high-heat proof and radiation proof are desired by many components, such as the steam condenser tubes, the irradiation targets for transmuting radioactive wastes and the overpacks for geological disposal of high level radioactive wastes (Setoyama et al. 2004).

Titanium is the preferred choice for surgical instrumentation due to its lighter weight, bacterial resistance and durability. High strength-to-weight ratio, corrosion resistance, non-toxic state and non-ferromagnetic property has made titanium "the metal of choice" within the field of medicine. It is also durable and long-lasting.

When titanium cages, rods, plates and pins are inserted into the body, they can last for more than 15 years. And dental titanium, such as titanium posts and implants, can last even longer. Osseo integration is a unique phenomenon where the body's natural bone and tissue actually bonds to the artificial implant. This firmly anchors the titanium dental or medical implant into place. Titanium is the only metal that allows this integration. Titanium and its alloys are widely used to replace failed hard tissues, such as artificial hip joints and dental implants (Li et al. 2008). Mechanical properties such as high strength, ductility and fatigue resistance, as well as a low modulus make titanium and its alloy suitable for applications in jet propulsion systems and human body implant (Heinrich et al. 1996). Titanium has long been used as an implant material in different medical applications, showing excellent performance in forming a close contact to the surrounding tissues (Petersson et al. 2009).

1.4.6 Iron

Pure iron is silvery metal with a shining surface. It is a good conductor of heat and electricity. Iron is used to make bridges, automobiles and support for buildings, machines and tools. It is mixed with other elements to make alloys, the most important of which is steel (Sparrow 1999).

Iron-based glassy alloys seem to be one of the most interesting materials due to their soft magnetic properties including high-saturation magnetisation. They are suitable materials for many electrical devices such as electronic measuring and surveillance systems, magnetic wires, sensors, band-pass filters, magnetic shielding, energy-saving electric power transformers (Nowosielski et al. 2008).

1.4.7 Nickel

Nickel is a silvery-white lustrous metal with a slight golden tinge. It is one of the four ferromagnetic elements that exist around room temperature, the other three being iron, cobalt, and gadolinium. Its Curie temperature is 355°C. Nickel is non-magnetic above this temperature (Kittel 1996). Nickel belongs to the transition metals and is hard and ductile. The isotopes of nickel range from ^{48}Ni to ^{78}Ni. The isotope of nickel with 28 protons and 20 neutrons ^{48}Ni is "double magic" and therefore unusually stable (Audi 2003).

The metal is corrosion-resistant, finding many uses in alloys, as plating, in the manufacture of coins, magnets, common household utensils, rechargeable batteries, electric guitar strings, as a catalyst for hydrogenation, and in a variety of other applications. Enzymes of certain life-forms contain nickel as an active centre, which makes the metal an essential nutrient for those life-forms. It is also used for plating and as a green tint in glass. In the laboratory, nickel is frequently used as a catalyst for hydrogenation. Nickel is often used in coins, or occasionally as a substitute for decorative silver.

Rechargeable nickel batteries are one type of alkaline storage cylindrical battery and classified as secondary batteries.

Nickel battery has a positive electrode made of active material-nickelous hydroxide. Because of the perfectly, sealed construction and the efficient charge/discharge characteristics, nickel batteries provide superior features and practical values in long service life, high-rate discharge and stable performance. As a result, they are widely used in many fields such as communication and telephone equipment, office equipment, tools, toys and emergency devices and consumer applications.

A typical jet engine today contains about 1.8 tonnes of nickel alloys and includes a long list of tailor-made nickel-based-alloys to meet specific needs (Nickel Magazine 2007). Pure nickel is a strong candidate for protective coating in biodiesel storage applications, due to its high resistance to the corrosive nature of

biodiesel and its vapors and minimal catalytic effects on the oxidation of biodiesel (Boonyongmaneerat et al. 2011).

1.4.8 Copper

Copper is a ductile metal with very high thermal and electrical conductivity. Pure copper is rather soft and malleable, and a freshly exposed surface has a pinkish or peachy color. It is used as a thermal conductor, an electrical conductor, a building material, and a constituent of various metal alloys.

Copper is the most widely used metal because of high conductivity. Copper and copper-based alloys are unique in their physical and mechanical properties. They have excellent corrosion resistance, high resistance to fatigue and relative ease of joining by soldering available in wide variety of forms (Pillai 2007).

Copper is easily worked, being both ductile and malleable. The ease with which it can be drawn into wires makes it useful for electrical work in addition to its excellent electrical properties. Copper can be machined, although it is usually necessary to use an alloy for intricate parts, such as threaded components, to get really good machinability characteristics. Good thermal conduction makes it useful for heat sinks and in heat exchangers. Copper has good corrosion resistance; it has excellent brazing and soldering properties and can also be welded, although best results are obtained with gas metal arc welding (Sambamurthy 2007). Copper as both metal and pigmented salt has a significant presence in decorative art.

1.4.9 Zinc

Zinc compounds are actively investigated because of their significant properties. Zinc oxide, being an *n*-type semiconductor with a wide direct gap of about 3.2 eV, has received much attention as a low-cost material for transparent and conductive films (Futsuhara et al. 1998). Zinc phosphide a II–V compound exists as a *p*-type semiconductor with a direct gap of near 1.51 eV, and is a promising low-cost material for solar cells due to its band structure (Pawlikowski 1981).

Zinc provides immunity, fertility and the capacity of senses including sight, taste and smell, notes the International Zinc Association. Zinc can also be recycled indefinitely, without losing any of its structural or functional characteristics (http://www.livestrong.com/article/199141-uses-for-zinc-powder/).

Zinc-air batteries (non-rechargeable) and zinc-air fuel cells (mechanically rechargeable) are electro-chemical batteries powered by oxidizing zinc with oxygen from the air. These batteries have high-energy densities and are relatively inexpensive to produce. Sizes range from very small button cells for hearing aids, larger batteries used in film cameras that previously used mercury batteries, to very large batteries used for electric vehicle propulsion.

In operation, a mass of zinc particles form a porous anode, which is saturated with an electrolyte. Oxygen from the air reacts at the cathode and forms hydroxyl ions which migrate into the zinc paste and form zincate, releasing electrons to travel to the cathode. The zincate decays into zinc oxide and water returns to the electrolyte. The water and hydroxyls from the anode are recycled at the cathode, so the water is not consumed. The reactions produce a theoretical 1.65 V, but this is reduced to 1.4–1.35 V in available cells. Zinc-air batteries have some properties of fuel cells as well as batteries, with zinc as the fuel, the reaction rate can be controlled by varying the air flow, and oxidised zinc/electrolyte paste can be replaced with fresh paste. Metallic zinc could be used as an alternative fuel for vehicles, in a zinc-air battery (Noring et al. 1993). Zinc-air batteries are considerably more safer in combating situations and more environmental friendly than lithium batteries (http://www.defense-update.com/products/z/zinc-air-battery-new.htm).

A Switzerland-based company, ReVolt uses zinc-air battery technology for hearing aids. ReVolt's battery claims to store three times more energy than lithium–ion by volume, and could incur just half the costs (http://www.goodcleantech.com/2009/11/a_powerful_rechargeable_zinc-a.php).

1.4.10 Tin

As the trend towards further miniaturisation of electronic products continues apace, packaging technology has progressed from the conventional wire and tape automated bonding to area array flip-chip bonding, which is able to provide increased input/output (I/O) counts and improved electrical performance (Qin et al. 2010). The advantages of this technology include high-density bonding, improved self-alignment, reliability and ease of manufacture (Wolf et al. 2006). One major step in the flip-chip interconnection process routes involves the deposition of, normally, solder alloys onto the bond pads of the chips (also known as solder bumping). With respect to the bumping materials, lead–tin-based alloys were the most widely used solders for flip-chip applications because of their low cost, low-melting point and excellent solderability properties. However, with world-wide legislation for the removal/reduction of lead and other hazardous materials from electrical and electronic products, development of a large number of lead-free, mostly tin-rich, alternative solders has been undertaken (Eveloy et al. 2005). Typically containing more than 90 wt% Sn, with a wide range of alloying elements such as Ag, Cu, In, Bi and Zn, these lead-free alternatives can be binary, ternary and even quaternary alloys, with variations in compositions. Sn–Ag–Cu solders can promote enhanced joint strength and creep and thermal fatigue resistance, and permit increased operating temperatures for advanced electronic systems and devices (Fabio and Mascaro 2006).

In electronic/optoelectronic packaging, chip bonding serves three major functions, i.e., mechanical support, heat dissipation and electrical connection (Hunziker et al. 1996). The choice of solder material for bonding is based on optimisation of a

number of properties, including solderability, melting temperature, Young's modulus (or stiffness), coefficient of thermal expansion, Poisson's ratio, fatigue life, creep rate and corrosion resistance. In terms of melting temperature, solders are typically classified as either hard (high-melting temperature) or soft (low-melting temperature). The Pb/Sn system is an example of a soft solder, which is commonly used for electronic packaging. Hard solders, e.g., Au/Sn, are used for optoelectronic packaging. Au/Sn solder, with its combination of good thermal and electrical conductivities, is particularly attractive for 'flip-chip' bonding, where the active area of the device is next to the submount. Au-20 wt% Sn is the most common composition utilised; it has a relatively high-melting temperature (280°C), good creep behaviour and good corrosion resistance (Ivey 1998).

Guide wires, catheters, stents, etc., are being increasingly employed in the diagnosis and treatment of cancer, diseases of the circulatory system, etc. A guide wire is used for navigating a catheter, a tube made of plastic, in a blood vessel. The tip portion of the guide wire must be sufficiently flexible to pass through the meandering blood vessels. On the other hand, in the body portion of the guide wire, a high-elastic modulus and strength against bending are also required to overcome the high resistance to bending and rotation in a blood vessel and to smoothly transmit the torque from the end to the tip of the guide wire (Sutou et al. 2006). Ti–Mo–Sn alloy is found to be a promising biocompatible material for use in catheters (Maeshima and Nishida 2004).

1.4.11 Tellurium

Due to the remarkable physical properties of tellurium such as low band gap and transparency in the infrared region, Te is used extensively in various technological areas. Te thin films find use in microelectronic devices such as gas sensor (Shashwati et al. 2004; Tsiulyanu et al. 2004) and optical information storage (Josef et al. 2004). Tellurium-based thin films, suitable for applications in environmental monitoring with considerably short-response time and high sensitivity to nitrogen dioxide at room temperature have been reported (Tsiulyanu et al. 2001).

Tellurium, with a low band gap of 0.32 eV, is one of the most promising materials for a shield in a passive radiative cooling (Engelhard et al. 2000). Radiative cooling is the one among today's challenges in materials science research. It occurs when a body gets cold by loosing energy through radiative processes. The phenomenon of radiative cooling uses the fact that the thermal energy emitted by a clear sky in the "window region" (8–13 mm) is much less than the thermal energy emitted by a blackbody at ground air temperature in this wavelength range. Hence, a surface on the earth facing the sky experiences an imbalance of outgoing and incoming thermal radiation and cools to below the ambient air temperature. While this concept can work well at night, assuming a

relatively dry atmosphere, the solar energy input during the day, which is normally much greater than that radiated out, causes heating of the system. To prevent this, a shield is required to cover the radiating surface in order to block solar radiation during the day as well as to prevent convective mixing in the cooled space. An ideal radiation shield should completely reflect solar radiation, but allow complete transmission in the "atmospheric-window" region. Solar radiation should preferably be reflected, as any absorbed radiation will be converted to heat somewhere in the system (Dobson et al. 2003). The different approaches for the design of shield are the introduction of optical scattering materials into shield substrates, and coating of shield substrates with high-solar reflector films. Te thin films with thickness of 111–133 nm having high-IR transmission across the full 8–13 μm band region suitable for solar radiation shield devices have been prepared by chemical vapor deposition method (Tian et al. 2006). Tellurium is used in photocopiers to enhance picture quality.

1.5 Significance of Alloys

Technology is reshaping our day-to-day life. Metals and their alloys make today's manufacturing industry, agriculture, construction and communication systems, transportation, defense equipments, etc., possible. Our manufacturing industries are using different metals and alloys as raw materials for their finished goods.

There are a large number of possible combinations of different metals and each has its own specific set of properties. Alloying one metal with other metal or non-metal often enhances its properties. For example, steel is stronger than iron, its primary element. The physical properties, such as density, reactivity, Young's modulus and electrical and thermal conductivity, of an alloy may not differ greatly from those of its elements, but engineering properties, such as tensile strength (Francis 2008) and shear strength may be substantially different from those of the constituent materials. This is sometimes due to the size of the atoms in the alloy, since larger atoms exert a compressive force on neighboring atoms, and smaller atoms exert a tensile force on their neighbors, helping the alloy resist deformation. Sometimes alloys may exhibit marked differences in Behaviour even when small amounts of one element occur (Hogan 1969; Zhang and Suhl 1985). Some of the major reasons for the continuing advances in alloys are the availability of materials, new manufacturing techniques, and the ability to test alloys before they are ever produced. Most modern alloys are, in fact, preplanned using sophisticated computer simulations, which help determine what properties the alloy will display.

1.5.1 Alloys in Nuclear Reactors

Structural materials employed in reactor systems must possess suitable nuclear and physical properties and must be compatible with the reactor coolant under the conditions of operation. The most common structural materials employed in reactor systems are stainless steel and zirconium alloys. Zirconium alloys have favourable nuclear and physical properties (Kutty et al. 1999), whereas stainless steel has favourable physical properties. Aluminium is widely used in low-temperature test and research reactors; zirconium and stainless steel are used in high-temperature power reactors. Zirconium is relatively expensive, and its use is therefore confined to applications in the reactor core where neutron absorption is important.

1.5.2 Alloy Wheels

Alloy wheels are automobile (car, motorcycle and truck) wheels which are made from an alloy of aluminium or magnesium (or sometimes a mixture of both). They are typically lighter for the same strength and provide better heat conduction and improved cosmetic appearance. Lighter wheels can improve handling by reducing vehicle mass which helps to reduce fuel consumption. Better heat conduction can help dissipate heat from the brakes, which improves braking performance in more demanding driving conditions and reduces the chance of brake failure due to overheating (Nunney 2006). Alloy wheels are also purchased for cosmetic purposes as the alloys used are largely corrosion-resistant. This permits the use of attractive bare-metal finishes, with no need for paint or wheel covers, and the manufacturing processes allow intricate, bold designs. Magnesium alloy wheels, or "mag wheels" are sometimes used on racing cars, in place of heavier steel or aluminium wheels, for better performance.

1.6 Significance of the Alloys Dealt With in this Research Work

Some of the commercially and industrially important metals and alloys have been analyzed in this work and their significance are discussed briefly in the following lines.

1.6.1 Cobalt Aluminium

Intermetallic alloys, including CoAl and NiAl, are of great importance since these materials not only have good strength-to-weight ratio but also has excellent corrosion and oxidation resistance, which make them good candidates for high-

temperature and soft magnetic applications (Wan et al. 2010). Among the intermetallics, Cobalt aluminides are of a considerable technological interest for high-temperature applications (Lee et al. 2004). Cobalt forms a stable B2 (CsCl) structure with Al in a wide concentration range (Botton et al. 1996). This structure can be considered as two interpenetrating primitive cubic sublattices, where each Co atom has eight Al atoms as nearest neighbors and vice versa. Depending on the concentration, CoAl alloys exhibit different mechanical and magnetic properties (Kudryavtsev et al. 1998). CoAl is especially attractive for epitaxial growth due to its low lattice mismatch with respect to GaAs (Wan et al. 2010). In combination with semiconductor hetero structures, they are able to be integrated in a number of devices, e.g., spin injectors and mirrors.

Cobalt-based super alloys consume most of the produced cobalt. The temperature stability of these alloys makes them suitable for use in turbine blades for gas turbines and jet aircraft engines. Cobalt-based alloys are also corrosion and wear-resistant. Cobalt-based alloys are used in total joint replacement applications where high strength and corrosion resistance are necessary. Special cobalt–chromium–molybdenum alloys are used for prosthetic parts such as hip and knee replacements (Michel et al. 1991). Cobalt alloys are also used for dental prosthetics, where they are useful to avoid allergies to nickel. Some high-speed steels also use cobalt to increase heat and wear-resistance. The special alloys of aluminium, nickel, cobalt and iron, known as Alnico, are used in permanent magnets (Luborsky et al. 1957).

1.6.2 Nickel Aluminium

NiAl, an intermetallic compound, is a promising material for aerospace applications. It has a combination of important structural properties, such as high mechanical strength, low density, high-melting point, high thermal conductivity and excellent oxidation resistances (Choudry et al. 1998; Ng et al. 1997). It has potential applications such as hot sections of gas turbine engines for aircraft propulsion systems, coats under thermal barrier coating, electronic metallisation compounds in advanced semiconductors and surface catalysts (Albiter et al. 2002). Strong bonding between aluminium and nickel, which persists at elevated temperatures yields excellent high-temperature properties and specific strength that are competitive with those of super alloys and ceramics. Thus, these alloys offer new opportunities for applications in gas turbines at temperatures higher than those currently possible with conventional nickel-based super alloys. The advantages of NiAl-based intermetallics are a high-melting point above 1,460°C and high thermal conductivity. Due to their excellent high-temperature properties NiAl-based intermetallics are potential candidate materials for combustion chambers heat shields and first row vanes in industrial gas turbines (Scheppe et al. 2002). Polycrystalline NiAl exhibits a brittle–ductile transition at temperatures ranging from 300 to 600°C which are significantly lower than those of other intermetallic

compounds. These properties have made NiAl-based alloy a promising candidate in some high-temperature (HT) structural applications (Gaoa et al. 2005).

Fine grains of a nickel-aluminium alloy, known as Raney nickel are used in many industrial processes. It is used as a heterogeneous catalyst in a variety of organic syntheses, most commonly for hydrogenation reactions. Its structural and thermal stability (i.e., the fact that it does not decompose at high temperatures) allows its use under a wide range of reaction conditions (Carruthers 1986). Raney nickel is used in a large number of industrial processes and in organic synthesis because of its stability and high-catalytic activity at room temperature (Hauptmann and Walter 1962).

1.6.3 Nickel Chromium

Nichrome wire, an alloy typically made of 80% nickel and 20% chrome, has specific characteristics that make it ideal for certain uses. It is silvery-grey in color, is corrosion resistant and has a high-melting point of about 1,400°C. Its ability to conduct electricity, withstand heat, its strength, flexibility and melting point determine its uses and applications.

Nichrome wire is used to make coils for heating elements. Due to its relatively high resistivity and resistance to oxidation at high temperatures, it is widely used in heating elements, such as in hair dryers, electric ovens, toasters and irons. Industrial uses include a wide variety of heating elements for ovens of all sizes, and devices that must apply heat directly to surfaces, such as for sealing plastic packages. Medical laboratories use nichrome wire loops somewhat like small spoons for handling specimens because they withstand frequent and repeated sterilisation, then cool rapidly. In industrial use, fine nichrome wire meshes serve as filters for liquids at high temperatures. Since the wire heats up rapidly with even a small amount of electricity, it makes safe igniters (sometimes called electric matches) to light the fuses of fireworks and model rockets. A piece of nichrome wire about an inch-and-a-half long connected to a length of lead wire allows the operator to safely detonate the device from a distance with only a battery and a switch. Fireworks professionals use nichrome igniters with timers at large displays. NiCr thin films are widely used in several applications in microelectronics such as thin film resistors, filaments and humidity sensors because of their relatively large resistivity, more resistant to oxidation and a low-temperature coefficient of resistance (Kwon et al. 2005). $Ni_{80}Cr_{20}$ matrix offers excellent high-temperature oxidation/corrosion resistance and essential mechanical strength (Ding et al. 2007). For dental clinical applications, the NiCr-based casting alloys are developed as an alternative to gold-based alloys due to their corrosion resistance in oral environment (Huang 2003). Nichrome $Ni_{80}Cr_{20}$ wt% films are used for strain gauge applications because of their high resistivity, low-temperature coefficient of resistance, commercial availability and low-temperature dependence of gauge factor (Chen et al. 2008).

1.6.4 Iron–Nickel

Iron group metals and binary alloys have a number of important industrial applications (Fabio and Mascaro 2006). Fe–Ni alloys have attracted much attention due to their interesting mechanical and magnetic properties (Karayannis and Moutsatsou 2006). Permalloy is a Fe–Ni alloy used in soft magnetic read/write heads (Cacciamani et al. 2010). Fe–Ni-based alloy powders are interesting in their applications as soft magnetic materials with low coercivity and high permeability (Gheisari et al. 2009).

One of the important challenges of electrical motors is to increase the efficiency to obtain more power with the same electrical energy consumed. The use of iron–nickel alloys increases the efficiency by reducing the magnetic losses significantly (Frederic et al. 2007). Fe–Ni thin films and multilayered structures are materials for high-frequency devices, such as inductors or magneto impedance effect (MI)-based magnetic field sensors (Kurlyandskaya et al. 2011).

Typical applications that are based on the low coefficient of thermal expansion of Fe–Ni alloys include thermostatic bimetals, glass sealing, integrated circuit packaging, cathode ray tube shadow masks, composite molds/tooling and membranes for liquid gas tankers (Cacciamani et al. 2010). Applications based on the soft magnetic properties include read-write heads for magnetic storage, magnetic actuators, magnetic shielding and high-performance transformer cores. Due to their unique low coefficient of thermal expansion and soft magnetic properties, Fe–Ni alloys are used in several industrial applications (McCrea et al. 2003).

1.6.5 Sodium Chloride Doped with Silver

Silver alkali halides provide interesting model systems for the study of decomposition processes in ionic solids. This is not only due to the absence of structural phase transitions but also due to the invariance of the anion sublattice, which is not involved in the demixing process. The phase separation is entirely confined to the cationic system and the anions exhibit an almost rigid frame. Along with the strong polarizability of silver ions, this feature guarantees that even single crystals are not destroyed during demixing (Elter et al. 2005). The dynamics of $Na_{1-x}Ag_xCl$ show that in the homogeneous phase, the doping of NaCl with silver ions leads to a considerable softening of the lattice (Caspary et al. 2007).

Semiconductors in confined surroundings experience a very significant development considering their importance in optoelectronic technologies. The semiconductors concerned are those having a direct and wide band gap conferring them with a radiative character and consequently a rather considerable output of photoluminescence, contrary to indirect gap semiconductors with a weaker output. Photosensitivity is observed in ionic semiconductors such as sodium chloride doped with silver (Madani et al. 2004).

1.6.6 Aluminium Doped with Iron

The addition of iron as a dopant in aluminium for integrated circuit applications substantially increases resistance to electro migration and creep. The amount of iron utilised depends to an extent on the electrical requirements of the device, the geometry of the device, the substrate composition and composition of overlying layers.

Stress-induced grain boundary movement in aluminium lines used as connections in integrated circuits are substantially avoided by doping aluminium with iron. Through this expedient not only is grain boundary movement is avoided but the electro migration problems are decreased (Ryan et al. 1993).

Aluminium doped with iron is distinguished by high thermal-shock resistance and, at temperatures of 800°C has comparatively good mechanical properties. It has mechanical properties which permit its use in components which are slightly stressed mechanically. It has excellent shock resistance and can therefore be used in those parts of thermal installations which are subject to frequent thermal cycling, such as in particular as a casing or casing part of gas turbine or of turbo charger or as a nozzle ring (Nazmy et al. 1995).

To meet the recent trends towards appealing, custom effects, many new effect pigments have been developed in the last few years in the automotive industry in recent past. Besides micas, flake-like particles have been doped with ultra thin layers of metal oxides and launched into coating markets. Aluminium flakes, doped with thin layers of iron oxide find much demand in this industry (Poth 2008).

1.7 Ball Milling

Most crystalline solids are composed of a collection of many small crystals or grains, termed polycrystalline. The term nano crystalline materials (Gleiter 1989) are used to describe those materials that have a majority of grain diameters in the typical range from 1 to 50 nm (McHenry and Laughlin 2000). The nano crystalline materials have received much attention as advanced engineering materials with unique physical and mechanical properties. The mechanical properties of the nano crystalline materials at room temperature have higher strength and toughness to those of coarse-grained ones (Gleiter 1981).

Nano crystalline materials can be successfully synthesised by several techniques, including inert gas condensation (Birringer et al. 1984), rapid solidification (Inoue 1994), sputtering (Li and Smith 1989), crystallisation of amorphous phases (Lu et al. 1995) and chemical processing (Kear and Strutt 1995). Among the different options for preparations, the ball milling method has been considered the most powerful tool for nanostructure materials because of its simplicity relatively inexpensive equipment and the possibility of producing large quantities that can be scaled up to several tons (Zhao et al. 2010).

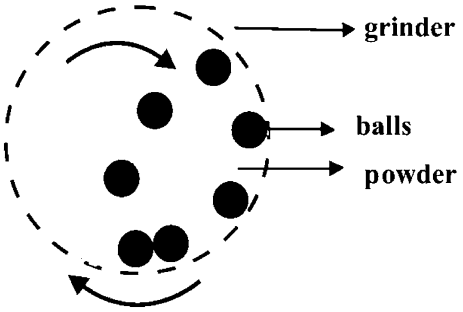

Fig. 1.2 Balls and powder sample in a ball mill

A ball mill is a type of grinder and a cylindrical device used in grinding (or mixing) materials like ores, chemicals and ceramic raw materials. Ball mills rotate around a horizontal axis, partially filled with the material to be ground and the grinding medium (Fig. 1.2). Different materials are used as media, including ceramic balls, alumina balls and stainless steel balls. An internal cascading effect reduces the material to a fine powder. Industrial ball mills can operate continuously fed at one end and discharged at the other end. Large-to-medium sized ball mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion) (Rajagopal 2009).

Ball mills are also used in pyrotechnics and the manufacture of black powder, but cannot be used in the preparation of some pyrotechnic mixtures such as flash powder because of their sensitivity to impact. High-quality ball mills are potentially expensive and can grind mixture particles to as small as 5 nm, enormously increasing surface area and reaction rates. The grinding works on principle of critical speed. The critical speed can be understood as the speed after which the balls (which are responsible for the grinding of particles) start rotating along the direction of the cylindrical device; thus causing no further grinding (Malik and Singh 2010). Ball mills are used extensively in the Mechanical alloying process in which they are not only used for grinding but also for cold welding as well, with the purpose of producing alloys from powders.

1.7.1 Mechanism for the Formation of Nano Crystalline Materials by the Ball Milling

The mechanism for formation of nano crystalline materials by the ball milling technique has been summarised as the phenomenology of the grain size reduction into three stages (Fecht 1995).

First stage: Plastic deformation is produced in the crystal lattices of the ball-milled powders by slip and twinning. This deformation is localised in shear bands containing a high-dense network of dislocation. The local shear instability of a

crystal lattice can be triggered by the material heterogeneity and enhance instabilities. These instabilities result from a non-uniform heat transfer during the mechanically induced deformation of the milled powders. During this stage of milling, the atomic level strain increases as a result of increasing the dislocation density.

Second stage: Due to the successive accumulation of the dislocation density, the crystals are disintegrated into sub-grains that are initially separated by low-angle grain boundaries. The formation of these sub-grains is attributed to the decrease of the atomic level strain.

Third stage: Further ball milling time leads to further deformation occurring in the shear bands located in the unstrained parts of the powders which leads to sub-grain size reduction so that the orientation of final grains become random in crystallographic orientations of the numerous grains and hence, the direction of slip varies from one grain to another.

In ball mills, the useful kinetic energy can be applied to the powder particles of the reactant materials by

- Collision between the balls and the powders (Fig. 1.2)
- Pressure loading of powders pinned between milling media or between the milling media and the liner
- Impact of the falling milling media
- Shear and abrasion caused by dragging of particles between moving milling media
- Shock wave transmitted through crop load by falling milling media.

1.7.2 Effect of Materials of Milling Media

There are many types of milling media suitable for use in a ball mill, each material having its own specific properties and advantages (Rajagopal 2009). Common in some applications are stainless steel balls. While usually very effective due to their high density and low contamination of the material being processed, stainless steel balls are unsuitable for some applications, such as black powder and other flammable materials require non-sparking lead, antimony, brass or bronze grinding media. In some applications ceramic or flint grinding media is used. Ceramic media are also very resistant to corrosive materials. High-density alumina media are widely used to grind clay bodies, frits, glazes and other ingredients. It is more expensive than silica media but is more efficient.

Fig. 1.3 Laboratory ball mill

1.7.3 Laboratory Ball Mill

The laboratory ball mill is a low-energy ball mill which is used in the present study. It is less expensive and operates with minimum maintenance requirements. The vial is a cylinder made of stainless steel with a radius of 2.5 cm. Stainless steel balls of different radii have been used as the milling media. The rotation speed is about 200 rpm. It produces homogenous and uniform powders. The laboratory ball mill used in our work is shown in Fig. 1.3.

1.8 X-Ray Diffraction

The modern understanding of metals and alloys, their structures, defects and various properties would not be possible if their crystal structures had not been revealed by XRD studies. XRD is a non-destructive technique for analyzing a wide range of materials, including crystals, metals, minerals, polymers, thin film coating and ceramics. Crystalline materials are characterised by the orderly, periodic arrangements of atoms. The unit cell is the basic repeating unit that defines a crystal. Parallel planes of atoms intersecting the unit cell are used to define directions and distances in the crystal. These crystallographic planes are identified by miller indices (Warren 1990). Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal.

XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$) (Bragg 1912). This law relates the wavelength of

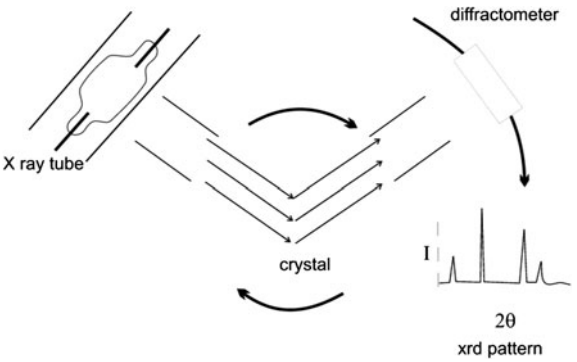

Fig. 1.4 Determination of crystal structure through X-rays

electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted.

Figure 1.4 illustrates how crystalline structure may be determined through XRD. As the crystal and detector rotate, X-rays diffract at specific angles. The detector reports the intensity (I) of X-ray photons as it moves. Angles of diffraction (where the Bragg equation is satisfied) are marked by peaks. The peak height is a function of the interaction of the X-rays with the crystal and the intensity of the source.

1.8.1 X-Ray Diffraction Methods

Classically, the two main ways of studying metals and alloys were metallography (the examination of polished and etched surfaces) and cooling curves (looking for discontinuities that indicated some sort of phase change). Both these methods involved considerable skill and experience, and the results were not always unambiguous. The introduction of XRD provided a much clearer, simpler and more objective way of investigation. XRD is now a common technique for the study of crystal structures and atomic spacing.

In terms of the specimen handled, two methods can be identified,

1. Powder diffraction
2. Single-crystal diffraction

In the former, the specimen is a collection of crystallites. Since these fragments are completely randomly oriented the incident X-ray beam meets with every possible lattice plane, oriented in all directions. Whereas in the single-crystal method, the whole specimen is a single piece, without any discontinuity in the lattice arrangements (Tareen and Kutty 2001). All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed to the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays.

1.8.2 Diffractometers

A typical X-ray diffractometer consists of a source of radiation (X-ray tube), a monochromator to choose the wavelength, slits to adjust the shape of the beam, sample and a detector. In a more complicated apparatus also a goniometer can be used for fine adjustment of the sample and the detector positions (Azaroff 1968).

1.8.3 Powder X-Ray Diffraction Instrumentation

The powder method essentially has two different ways of registering the diffracted X-rays (Tareen and Kutty 2001).

1. The whole diffraction pattern is recorded simultaneously on a photographic film called the powder photographic method.
2. The diffraction pattern is scanned by a counter device, or a solid-stated semiconductor detector. The counter or detector registers the diffracted beam in successive stages, away from the direct beam.

In X-ray diffractometers, X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towards a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$ (Stout and Jensen 1989). The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, and Cr). The monochromatic radiation required for the powder method is usually the $K_{\alpha 1 \alpha 2}$ doublet, monochromated by crystal reflection or by the use of a filter whose K absorption wavelength falls between the K_α and the K_β wavelengths. The Cu $K_{\alpha 1 \alpha 2}$ doublet ($\lambda = 1.542$ Å) with a Ni filter $\lambda_k = 1.488$ Å is probably used more than any other source (Warren 1990). These X-rays are collimated and directed onto the sample. The sample is mounted on a goniometer (Shirane et al. 2002) and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as reflections. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity is seen. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

1.8.4 Single-Crystal X-Ray Diffraction Instrumentation

The foremost essential criteria for single-crystal XRD are to obtain an adequate crystal of the material under study. The crystal should be sufficiently large (typically larger than 0.1 mm in all dimensions), pure in composition and regular in structure, with no significant internal imperfections such as cracks or twinning.

The crystal is placed in an intense beam of X-rays, usually of a single wavelength (monochromatic X-rays), producing the regular pattern of reflections. Molybdenum is the most common target material for single-crystal diffraction, with MoK_{α} radiation = 0.7107Å. These X-rays are collimated and directed onto the sample. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor. Modern single-crystal diffractometers use CCD (charge-coupled device) technology to transform the X-ray photons into an electrical signal which are then sent to a computer for processing.

Single-crystal diffractometers use either three- or four-circle goniometers. These circles refer to the four angles (2θ, χ, φ, and Ω) (Shirane et al. 2002) that define the relationship between the crystal lattice, the incident ray and the detector as shown in Fig. 1.5. Samples are mounted on thin glass fibers using an epoxy or cement. The thin glass fiber is attached to brass pins and mounted onto goniometer heads. The goniometer head and sample are then affixed to the diffractometer. Samples are centered by viewing the sample under an attached microscope and are placed under the cross-hairs for all crystal orientations. Once the crystal is centred, a preliminary rotational image is often collected to screen the sample quality and to select parameters for later steps. As the crystal is gradually rotated, previous reflections disappear and new ones appear, the intensity of every spot is recorded at every orientation of the crystal. Multiple data sets may have to be collected, with each set covering slightly more than half a full rotation of the crystal and typically containing tens of thousands of reflections (Massa 2004).

An automatic collection routine can then be used to collect a preliminary set of frames for determination of the unit cell. Reflections from these frames are auto-indexed to select the reduced primitive cell and calculate the orientation matrix (which relates the unit cell to the actual crystal position within the beam). These data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal and converted to the appropriate crystal system and Bravais lattice (Giacovazzo 2002). The final, refined model of the atomic arrangement is the essential crystal structure.

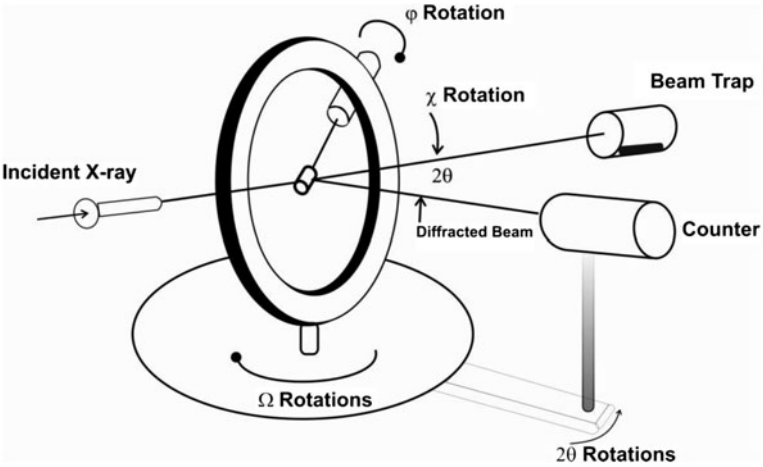

Fig. 1.5 Goniometer

1.8.4.1 Corrections for Background, Absorption

After the data have been collected, corrections for instrumental factors, polarisation effects of X-ray absorption (Glusker et al. 1994) and (potentially) crystal decomposition must be applied to the entire data set. This integration process also reduces the raw frame data to a smaller set of individual integrated intensities. These correction and processing procedures are typically part of the software package which controls and runs the data collection.

Single-crystal XRD is most commonly used for precise determination of a unit cell, including cell dimensions and positions of atoms within the lattice. Bond-lengths and angles are directly related to the atomic positions. A single, robust, optically clear sample, generally between 50 and 250 microns in size is essential. Data collection generally requires between 24 and 72 h.

1.9 Grain Size Analysis from X-Ray Diffraction

The size of the grains in a polycrystalline material has more effect on the properties of the material, for example, the hardness of a metal or alloy increases with decrease in the grain size (Cullity and Stock 2001). This dependence of properties on grain size makes the measurement of grain size important in the control of most metal forming operations.

In this book the grain size has been reported for some metals which has been analyzed from XRD. The grain morphology was examined by SEM. The software GRAIN written by Dr.R.Saravanan was used to estimate approximate grain sizes from XRD (Saravanan, GRAIN software). The grain size is analyzed using full

width at half maximum of the powder XRD peaks. The Debye–Scherrer formula given in Eq. 1.1has been used to calculate the particle size.

$$\tau = \frac{K\lambda}{\beta \cos\theta} \tag{1.1}$$

where K is the shape factor, λ is the X-ray wavelength, typically 1.54 Å, β is the line broadening at half the maximum intensity (FWHM) in radians and θ is the Bragg angle (Patterson 1939) τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than about 0.1 μm, which precludes those observed in most metallographic and ceramographic microstructures.

It is important to realise that the Scherrer formula provides a lower bound on the particle size. The reason for this is that a variety of factors can contribute to the width of a diffraction peak; besides particle size, the most important of these are usually inhomogeneous strain and instrumental effects. If all of these other contributions to the peak width were zero, then the peak width would be determined solely by the particle size and the Scherrer formula would apply. If the other contributions to the width are non-zero, then the particle size can be larger than that predicted by the Scherrer formula, with the "extra" peak width coming from the other factors.

1.10 Scanning Electron Microscope

The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens (Malik and Singh 2010). The signals derived from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a two-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50–100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure and crystal orientations (Reimer 1998).

SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Backscattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped

with diffracted backscattered electron detectors (EBSD) can be used to examine microfabric and crystallographic orientation in many materials.

1.11 Fundamental Principles of Scanning Electron Microscopy

Accelerated electrons in SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals are produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence-CL) and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples, secondary electrons are most valuable for showing morphology and topography of samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e., for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam (Goldstein 2003).

SEM analysis is considered to be "non-destructive", i.e., X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

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